1-15-43

PURE
NICKEL NEON
SIGN ELECTRODES
LAST LONGER, PER-
FORM BETTER YET
COST NO MORE. PURE
NICKEL NEON SIGN
ELECTRODES LAST
LONGER, PERFORM
BETTER COST NO
MORE. PURE
NICKEL
NEON

A discussion of the technical characteristics of pure nickel electrode shells which account for their better performance and longer life.

Pure nickel electrodes are made by

EYELET SPECIALTY COMPANY

WATERBURY, CONNECTICUT

And sold through the usual sources of supply

SKILL + GLASS TUBING + RARE GAS + GOOD ELECTRODES =

GOOD SIGNS

Years of experience have given you the skill; - high quality tubing and rare gases are sold by reliable manufacturers - but what do you know about your electrodes? You have been told of the horrors of "sputter factor", amalgamation, porous metals (whatever that may mean) so much that electrodes have become something of a nightmare. Now it is time to look into the facts concerning metals which are important to you.

WHAT GOES ON AT THE ELECTRODES?

An electrode leads a double life, for it is alternately cathode and anode and must perform well in both roles. The voltage drop at the anode is low for most metals and the anode occasions little concern, but the cathode leads a hard life, for it is bombarded by ions or positively charged atoms of rare gas or mercury traveling at high speed, and its behavior determines the life of the tube. The speed of these ions increases with the voltage drop occurring near the cathode (the so-called "cathode fall") and if the ions hit hard enough they may knock off a small amount of metal from the electrode itself, which may remain within the electrode or escape to the nearby wall. This action, called "sputtering", goes on at a measurable rate only under conditions far removed from sign tube operation. Cathode drops of 1,000 volts or more and very low gas pressures (usually about .1 mm) are required and at these high cathode falls cadmium, silver, gold and copper sputter rapidly, nickel and iron much more slowly and zinc, aluminum and magnesium least. It seems probable that the presence of traces of oxygen producing a thin, highly protective film are responsible for the low sputtering rates of the latter elements and that if oxygen were completely absent they would sputter much faster. The rates of sputtering decrease rapidly with a decrease in cathode fall and there has been some question as to whether any sputtering occurred under normal sign tube operating conditions where the cathode fall is only 70 - 150 volts.

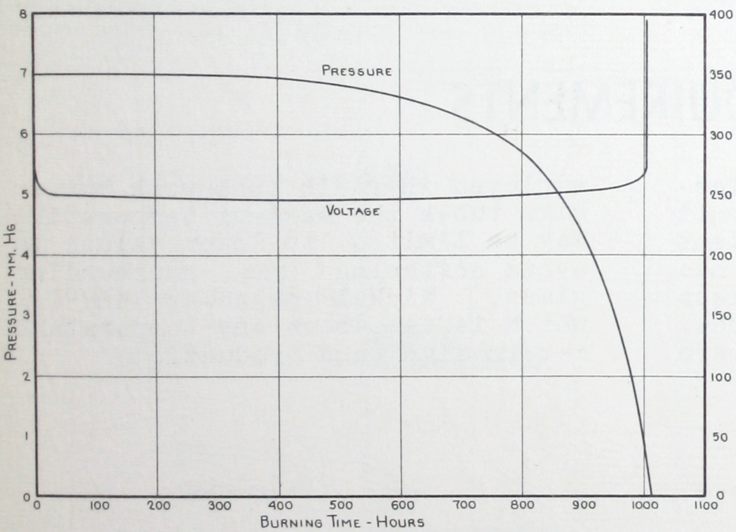
WHAT HAPPENS TO THE RARE GAS?

The direct effect of any sputtering which might occur in a sign tube is relatively unimportant, but it has been assumed that sputtered metal adsorbed rare gas and caused the tube to become hard and finally to cease operating, which would be important if true. This assumption has been found to be incorrect by H. Alterthum and his co-workers at the Osram Lamp Works in Berlin who performed a series of extremely careful experiments principally with hollow iron electrodes and made the remarkable discovery that neon was actually driven into the metal electrode where it was locked up but could be recovered by dissolving the whole electrode. Of even greater importance was the conclusion that "sputtering" had nothing to do with this clean-up of neon - a conclusion of great importance to the sign industry as sputtering and gas clean-up have been considered to be associated phenomena.

In most of Alterthum's experiments the tubes were operated on alternating current, but in one

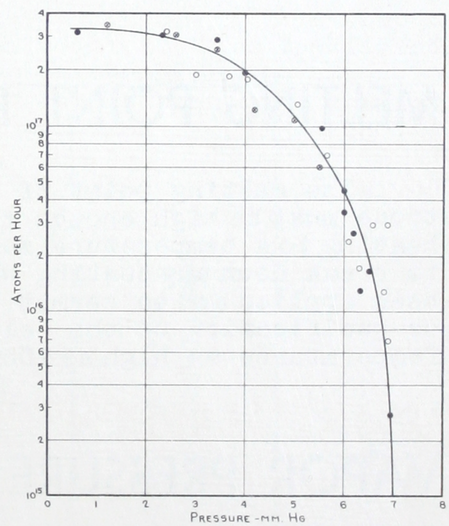
group of experiments the tubes were operated on direct current and the neon was found to be driven into the iron cathode. Generally, Pirani pressure gauges were fused directly to the discharge tubes and no stop cocks were present so that errors from leaks were absent; furthermore, extreme precautions were taken to really de-gas the iron electrodes by heating them in vacuo at least ten times by high frequency induction followed by bombarding up to ten times in a helium-neon mixture at low pressure. In view of these and other precautions their data must be accepted as reliable. The change in pressure with time in a small tube filled with neon and equipped with iron electrodes as determined in the above experiments is shown in Figure 1 and the rate at which atoms are driven into the iron electrodes and "cleaned up" at various pressures is shown in Figure 2. In this plot data from three sets of experiments are shown and the agreement is good evidence of the high quality of their work.

In view of the fact that the rate of "clean-up" at pressures below about 2 mm of mercury does not vary appreciably with the pressure as shown in Figure 2, further experiments were made in this pressure range to determine the relative time for electrodes of different materials to "clean-up" or "lock-up" a constant amount of neon. It was found that the life value of nickel was 112% that of iron, a fact which is obviously important to makers and users of sign tubes. These findings are confirmed by practical experience with small Xenon and Krypton tubes which are filled to a pressure of about 2 mm to secure useful brilliance and consequently are very hard on the electrodes. Of the many types of electrodes tried, uncoated nickel has proved to have the longest life.



Drop in Pressure with Time of Neon Tube with Iron Electrodes at 100 m.a.

FIG. 1



Effect of Pressure on Rate of "Clean-up" of Neon Tube with Iron Electrodes Operated at 100 m.a.

FIG. 2

COATED ELECTRODES

In many instances special coatings are applied to electrodes to increase the electron emission which results in lower electrode temperatures on bombardment and in a lower electrode drop in use. However, in tubes containing mercury, some coatings may increase the rate of darkening of the tube walls although special coatings have been devised which appear suitable for such tubes.

AMALGAMATION

In connection with mercury much has been said concerning amalgamation without distinguishing between wetting of the surface of the metal with mercury, as solder would wet any well-fluxed surface, and the possible soaking-in of mercury - which is a horse of a different color.

Copper is readily wetted with mercury which appears to "soak in" but nickel and iron are much more difficult to wet with mercury, although it can be done. Nickel and iron electrodes after long use in mercury-containing sign tubes were removed, wiped off and examined by a well-known chemist who reported no mercury in either electrode. It is evident from this result as well as from practical experience with solid nickel and nickel-plated iron shells that mercury does not soak into nickel.

Iron, if clean, can be amalgamated as is shown by the well-known experiment of breaking a piece of iron under mercury in which the freshly broken surface becomes amalgamated. Iron, nickel, tungsten and platinum can also be amalgamated by rubbing them with mercury containing a little sodium which serves as a flux, but as noted above neither nickel nor iron appear to absorb mercury. This is further demonstrated by commercial tubes equipped with nickel electrodes plus a rare gas and a very small amount of mercury which show no change in the amount of mercury on long use - indeed tubes of this type have been run as long as 40,000 hours without loss of mercury. The universal use of nickel in hot cathode mercury rectifiers is further evidence, if any be needed, of the excellent behavior of nickel in mercury tubes.

MELTING POINT REQUIREMENTS

The melting point of an electrode must be high enough to permit heating to a temperature sufficient to break down any coating which has been applied and to permit complete de-gasification of the electrode. Temperatures as high as 1050°C. are employed in radio tube work but in sign tubes the maximum temperature may be limited to lower values to avoid softening the surrounding glass. Nickel melts at 1450°C., which is far above any temperature met in sign tube production.

VAPOR PRESSURE

When metals are heated in vacuo they tend to sublime at a rate depending upon the vapor pressure of the metal at the temperature involved. Accurate determinations of the rates of sublimation and vapor pressure have been made by Jones, Langmuir and Mackay of the G. E. Research Laboratory which indicate that the vapor pressure of iron is slightly higher than that of nickel and that the vapor pressure of copper is 10 - 15 times that of nickel as shown in Table 1 where the volume of metal sublimed per second is also shown. Sublimation is of importance only in the production of tubes at which time the electrodes are highly heated, but is not important in subsequent operation, as the electrodes remain cool.

TABLE I

Temperature	Volume Rate of Evaporation		Vapor Pressure	
^oC	NICKEL cm sec^{-1}	IRON cm sec^{-1}	NICKEL mm Hg	IRON mm Hg
927	$2.25x10^{-10}$	$3.09x10^{-10}$	$1.56x10^{-7}$	$1.94x10^{-7}$
1027	$3.57x10^{-9}$	$4.94x10^{-9}$	$2.57x10^{-6}$	$3.22x10^{-6}$

GAS CONTENT OF ELECTRODES

The gas content of electrode metals is important and particularly the ease of removing such gas as may be present. The best available information on the gas content of nickel and iron is shown in Figure 3 and is the result of determinations made in the Research Laboratory of the General Electric Company and in one of the leading laboratories abroad. It may be noted that CO was the principal gas present in nickel whereas in iron, in addition to CO, considerable nitrogen was present which is very difficult to remove. It should be noted that these gases diffuse through the solid metal and that "porosity", whatever that may be, has nothing to do with it. A good surface finish is desirable in metals for sign tube and radio work and nickel is notable for its excellence in this respect. To those desiring to make sign tubes free from contaminating gases the importance of the low gas content of nickel is obvious.

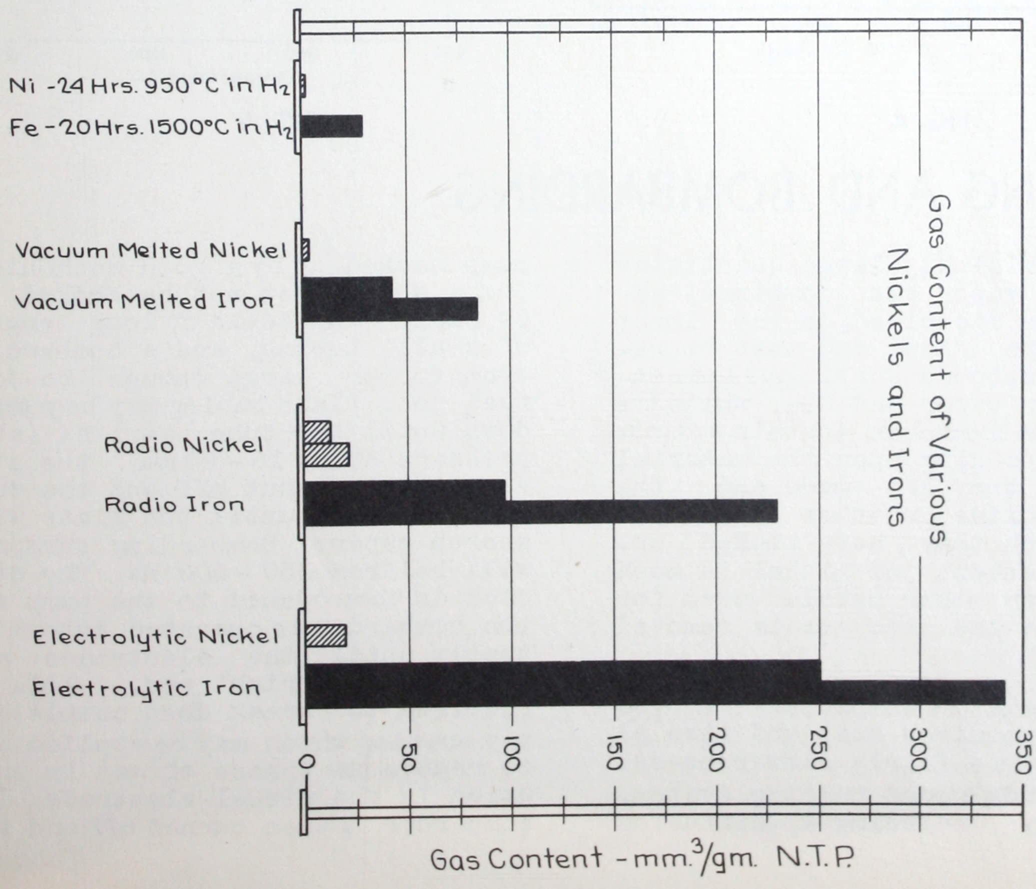


FIG. 3

SURFACE GAS + OXIDES

In addition to the gas within the metal, rust and other corrosion products are difficult to avoid with iron, and introduce additional foreign gas which requires pumping. Rust is particularly susceptible to sputtering which dirties up the tube near the electrode. The rate of oxidation or rusting of iron in a mild indoor atmosphere at 65°F. and 45% relative humidity as determined by Vernon is shown in Figure 4. He states that nickel remained perfectly bright for several months in this atmosphere. Some oxidation may also occur upon heating so that the relative rates of oxidation of nickel and iron are of some importance. As will be noted in Figure 5, iron oxidizes about 1,000 times as fast as nickel, the importance of which is self-evident.

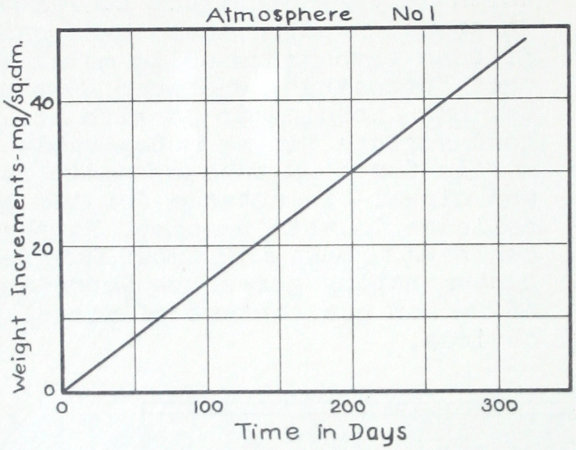


FIG. 4

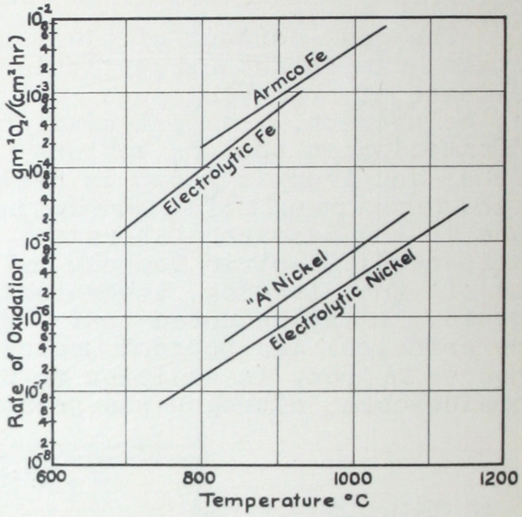


FIG. 5

PUMPING AND BOMBARDING

Surprisingly large quantities of water vapor are combined, adsorbed or dissolved on the inner wall of the glass and must be removed. Electrode coatings also contain water vapor and CO_2, while the electrodes themselves contain amounts of gas depending upon the material of which they are made and the amount of oxide or other contamination which they have picked up. The gas content of nickel is much lower than other metals used for electrodes and the gas is removed rapidly.

Gas must be completely removed and this requires heat and time as diffusion is a fairly slow process. This demands a good pumping system, preferably including a diffusion pump backed up by a good mechanical pump, which must not be choked up by small stop cocks or long lengths of small tubing, and a bombarding transformer large enough to do a real job. Plain tubing may be pumped down until the tube strikes (at a pressure about 15 - 20 mm), the stop cock is then shut off and the tube is bombarded until the glass will scorch paper. Bombarding currents will be from 350 - 500 Ma. The stop cock is then opened to the pump and the bombarder is operated intermittently until the electrodes are heated to a bright red. This is required to break down completely any coating which may be applied and to remove the traces of gas in solution in the nickel electrode. The bombarder is then turned off and the

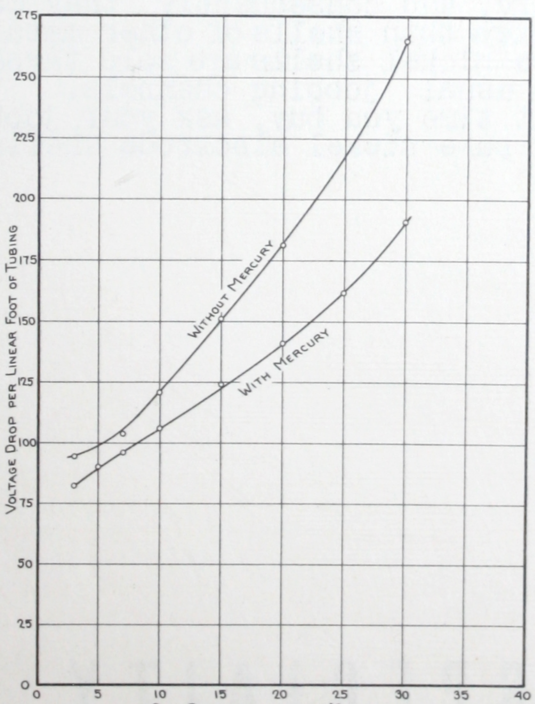
tube is allowed to cool until it can just be touched with the fingers. The pump stop cock is then turned off and the tube is filled with rare gas to standard pressure and sealed off.

When mercury is to be added it should be placed in a small side tube which is gently heated while the tube is cooling down on the pump. The heating should be sufficient to remove any gas from the side tube but should not cause the mercury to boil. The sign tube is then filled with a standard neon-argon or more complex mixture and sealed off. It is then aged to normal color and the mercury is run into the tube by inclining it. The mercury tube is then sealed off.

With fluorescent tubing, special care in pumping and bombarding is required to remove gas from the walls of the tube without damaging the fluorescent material. Bombarding generally may be done with air, preferably thoroughly dried, although some coatings require helium for bombarding. Where helium is used the tube is pumped down without bombarding and helium is introduced to a pressure of about 5 mm; bombarding is then done as described above. Helium has the valuable characteristics of being inert and possessing a high electrical resistance so that the tubing is easily heated to the temperature required.

Filling pressures for neon are fairly well standardized but some judgment is required with mixtures used with mercury, particularly when the tubing is required to operate at low temperatures. For the latter condition a slight increase in filling pressure is required or special gas mixtures giving a higher tube resistance may be used; the former is generally preferable.

Higher filling pressures increase the drop per foot of tubing, and thus increase its operating temperature -- this in turn increases the amount of mercury vaporized. The relation between filling pressure and voltage drop per foot is shown in Figure 6.



Voltage Drop per Foot of 12 mm. Tubing Filled to Various Pressures with B-10 Gas with and without Mercury

FIG. 6

From a consideration of the points covered on the preceding pages, it will be evident that pure nickel electrode shells are more satisfactory than those of other metals, both from the sign-maker's and the user's point of view. Make sure, however, that your shells are solid nickel -- nickel plated shells give you only the surface benefits of pure nickel. Pure nickel electrode shells perform better, just as sterling silver lasts longer and gives better service than plated ware.

We make pure nickel electrode shells in quantity on special machinery, and consequently they cost no more than shells of other metals. Pure nickel shells are sold through the usual jobbing channels. The next time you buy, ask your jobber for pure nickel electrode shells.

EYELET SPECIALTY COMPANY

WATERBURY, CONNECTICUT

PRINTED IN U. S. A.